The effect of artificial aging on Martens hardness and indentation modulus of different dental CAD/CAM restorative materials

Hampe, Rüdiger ; Lümkemann, Nina ; Sener, Beatrice ; Stawarczyk, Bogna

Abstract: OBJECTIVES To determine the Martens hardness parameters for five different classes of CAD/CAM restorative materials after storage in water and thermo-cycling. MATERIALS AND METHODS Lithium disilicate ceramic IPS e.max CAD (EX), silicate ceramic IPS Empress CAD (EC), a polymer infiltrated interpenetrating network material (hybrid material) VITA Enamic (VE), two compact filled composites Lava Ultimate (LU), experimental material (EM), two low filled resin composites Katana Avencia (KA), Ambarino High-Class (AH) and ultra-low/unfilled acrylic polymers CAD-Temp (CT), Telio CAD (TC), breCAM.HIPC (BC) were tested. Specimens were stored in water at 37 °C for 30, 60, 90, 120 days and afterwards thermo-cycled (30,000×, 5 °C/55 °C). Martens hardness (HM) and indentation modulus (E_{IT}) were longitudinally investigated after each storage time. For structural analysis, each material was analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). RESULTS The groups of unfilled polymers/ultra-low filled composite (CT, TC, BC) followed by low (KA, AH) and compact filled resin composites (LU, EM) showed the lowest HM and E_{IT} values ($p < 0.001$). The highest values presented ceramics (EX, EC) followed by hybrid material (VE) ($p < 0.001$). High influence on the Martens hardness parameters was exerted by the aging duration (HM: ${}_P{}^2 = 0.108$, $p < 0.001$; E_{IT}: ${}_P{}^2 = 0.074$, $p < 0.001$). Structural analyses of resin composites revealed big differences in shape, size and distribution of filler particles. CONCLUSIONS The tested CAD/CAM materials showed differences in Martens hardness and indentation modulus pursuant to the material class. Ceramics showed highest values, followed by the hybrid material. For resin composites the Martens hardness and indentation modulus increased with the filler content. Artificial aging affected CAD/CAM materials differently. Some materials tested are prone to aging, the Martens hardness and indentation modulus decreased after thermo-cycling.

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The effect of artificial aging on mechanical properties of different dental CAD/CAM restorative materials

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Short title: Martens hardness behavior of CAD/CAM restorative materials

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Highlights:

- Dental CAD/CAM restorative materials show very different mechanical properties
- Long term stability cannot be concluded from material class
- Thermo cycling reveals differences of CAD/CAM restorative materials and should be a mandatory part of artificial aging setups

Keywords:

Dental CAD/CAM restoratives, artificial aging, thermo cycling, Martens hardness, resin composite, ceramics

Abstract

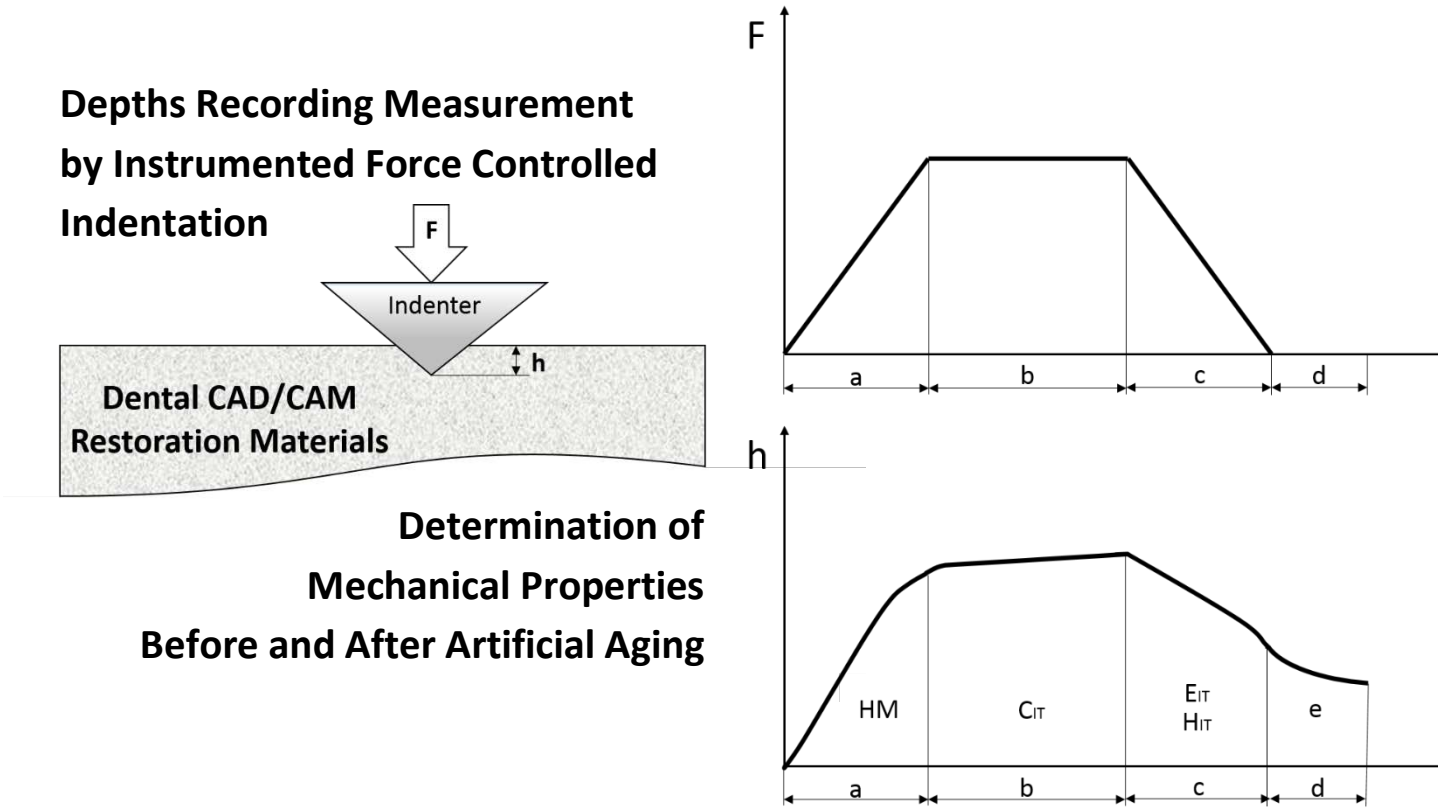
Objectives: To determine the Martens hardness parameter for five different classes of CAD/CAM restorative materials after storage in water and thermo cycling.

Materials and methods: Lithium disilicate ceramic IPS e.max CAD (EX), silicate ceramic IPS Empress CAD (EC), a polymer infiltrated interpenetrating network material (hybrid material) VITA Enamic (VE), two compact filled composites Lava Ultimate (LU), experimental material (EM), two low filled resin composites Katana Avencia (KA), Ambarino High-Class (AH) and ultra-low/unfilled acrylic polymers CAD-Temp (CT), Telio CAD (TC), breCAM.HIPC (BC) were tested. Specimens were stored in water at 37 °C for 30, 60, 90, 120 days and afterwards thermo cycled (30,000x, 5 °C/55 °C). Martens hardness (HM) and indentation modulus (E_{IT}) were longitudinally investigated after each storage time. For structural analysis, each material was analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

Results: The groups of unfilled polymers/ultra-low filled composite (CT, TC, BC) followed by low (KA, AH) and compact filled resin composites (LU, EM) showed the lowest HM and E_{IT} values ($p<0.001$). The highest values presented ceramics (EX, EC) followed by hybrid material (VE) ($p<0.001$). EX showed high density of distribution of crystallites, in contrast EC showed smaller crystallite structures and a higher content of an amorphous glass phase. VE showed smooth surface with massive flaws and volume defects, but filler particles were not apparent. Comparing the SEM images of resin composites revealed big differences in shape, size and distribution of filler particles.

Conclusions: The tested CAD/CAM materials showed different mechanical properties pursuant to the material class. Ceramics showed highest values, followed by the hybrid material. For resin composites the mechanical properties increased with the filler content. Artificial aging revealed different effects on materials. For some materials, the mechanical properties dropped down especially after thermo cycling.

Graphical Abstract



1 Introduction

Treatment options and materials used in dentistry progressed remarkably in the last years. The application of CAD/CAM (Computer aided design/computer aided manufacturing) technology contributes positively to comfortable and high quality dental services (Miyazaki et al. 2009). Patients are demanding esthetic restorations increasingly (Donovan, 2008). For indirect treatments, all ceramic restorations have been established as an esthetic metal free and long-term solution (Manhart et al., 2004; Ho&Matinlinna, 2011; Mangani et al., 2015). Resin composite restorations which can be manufactured using CAD/CAM technologies have been introduced as an alternative (Liebermann et al., 2016). These materials are rated as promising for the successful long-term use (Horvath 2016). On the other hand, the similarity in composition of some CAD/CAM resin composites and resin composites used for direct fillings raises the question whether these new CAD/CAM materials are also prone to degrade in oral environment as it has been shown for direct restorative materials (Ferracane, 2006; Borges et al., 2011). Due to the improved polymerization process compared to in situ curing of direct restorations, the manufacturers claim better and more constant restoration qualities (Mainjot et al., 2016). Regarding wear, all current CAD/CAM block materials behave similar or even better for permanent restorations than natural human enamel (Mörmann et al., 2013). Moreover, polymeric CAD/CAM materials are gentler to opposing teeth than ceramics (Stawarczyk et al., 2013). Considering the fracture load findings (Stawarczyk et al., 2012), polymeric CAD/CAM materials are also equivalent in performance to ceramic materials.

The success of a dental restoration treatment is defined by its longevity. The durability of resin composites can be substantially influenced by the oral environment (Almeida, 2010). When placed in the patient's mouth, restorations are exposed to a wet oral

environment which is physiologically characterized by natural saliva. Due to the significant role of moisture in the application of restoration materials, numerous investigations regarding the effects of moisture on mechanical performances of resin composites have been conducted in last decades (Manhart et al., 2004; Ferracane, 2006). Polymer networks particularly tend to be strongly influenced by wet oral environment (Munchow et al., 2014). Polymeric materials may alter their mechanical properties due to water uptake or elution of components (Ferracane, 2006; Borges et al., 2011) The results have revealed that almost all parameters of mechanical properties, such as flexural strength, hardness, and young's modulus decrease after storage in moist or wet conditions. Clinically, restorations are generally exposed to dynamic temperature fluctuation during routine breathing, eating and drinking. In general, temperature changes lead to residual stresses in solid materials (Morresi et al., 2014). The sensitivity of different mechanical properties of resin composite restorations to aging have also been investigated (Musanje et al., 2003; Ilie, 2005). Indentation techniques are an efficient way of testing mechanical properties at the surface that can be straight correlated to the morphology and the deformation behavior of materials (Bhandari et al., 2012). Instrumented indentation method is especially suitable to determine mechanical properties of materials (Shadad et al., 2007; Chicot&Tricoteaux 2010; ISO, 2002) and to detect surface degradations induced by aging (Bürgin 2017). Several relevant material parameters, e.g. Martens Hardness, indentation modulus – a parameter comparable with the Young's modulus, can be determined simultaneously in one measurement (ISO, 2002; Bhandari et al., 2012).

The aim of the present study is to evaluate the mechanical properties of dental CAD/CAM materials of 5 different material classes (glass-ceramic, hybrid material, compact filled composite, low filled composite, unfilled polymer or ultra-low filled

composites) and the influence of aging on these properties. The tested null hypotheses are: all material classes show similar mechanical properties, aging does not influence the mechanical properties of dental CAD/CAM materials.

2 Materials and Methods

Lithium disilicate ceramic IPS e.max CAD (EX), silicate ceramics IPS Empress CAD (EC), a polymer infiltrated interpenetrating network material VITA Enamic (VE) categorized as hybrid material, two compact filled composites Lava Ultimate (LU), experimental material (EM), two low filled resin composites Katana Avencia (KA), Ambarino High-Class (AH) and ultra-low/unfilled acrylic polymers CAD-Temp (CT), Telio CAD (TC), breCAM.HIPC (BC) were tested (Table 1).

Table 1. Summary of materials, abbreviations, compositions, manufacturers, and Lot numbers

Material Group	**Brand (LOT)**	**Manufacturer**	**Abbreviation**	**Composition***
Ceramics	IPS e.max CAD (M26697)	Ivoclar Vivadent, Schaan, Liechtenstein	EX	Lithium disilicate crystals ($Li_2Si_2O_5$) embedded in glass matrix
	IPS Empress CAD (T15789)		EC	Silicate crystals embedded in glass matrix
Hybrid	VITA Enamic (43000)	VITA Zahnfabrik, Bad Säckingen, Germany	VE	• Organic part: UDMA, TEGDMA** • Inorganic part: glass ceramic sintered network (86 wt%/75 V%)
Compact filled composites	Lava Ultimate CAD/CAM Restorative (N525997)	3M, St. Paul MN, USA	LU	• Organic part: UDMA** • Inorganic part: Silica (20 nm) and zirconia (4-11 nm) fillers and clusters (0.6-10 µm)

				thereof, filler amount of 79 wt%
	Experimental Material (b.28923)	Ivoclar Vivadent	EM	• Organic part: resin composite • Inorganic part: 80 wt% nanoparticles
Low filled composites	Katana Avencia (115)	Kuraray Noritake Dental, Tokyo, Japan	KA	• Organic part: UDMA, TEGDMA** • Inorganic part: 62 wt% aluminum oxide (20 nm), SiO_2 (40 nm)
	Ambarino High-Class (50712)	Creamed, Marburg, Germany	AH	• Organic part: Bis-GMA, UDMA, BDMA** • Inorganic part: 70.1% silicate glass fillers with size of 2-10 µm, average 0.8 µm
Unfilled polymers/ultra-low filled composite	VITA CAD-Temp (12430)	VITA Zahnfabrik	CT	• Organic part: PMMA**, pre-polymer spheres • Inorganic part: SiO_2** micro particle
	breCAM.HIPC (406700)	bredent, Senden, Germany	BC	• Organic part: PMMA, UDMA**
	Telio CAD (R36500)	Ivoclar Vivadent	TC	• Inorganic part: PMMA**

*according to manufacturer`s information

**UDMA: urethane dimethacrylate; TEGDMA: triethylenglycol dimethacrylate; Bis-GMA: bisphenol A glycidylmethacrylate; BDMA: butandiol dimethacrylate; SiO_2: Siliciumdioxide; PMMA: Polymethylmethacrylate

2.1 Specimen preparation

Specimens needed for microstructure analysis, element analysis, and mechanical properties analysis (N = 60; n = 6 per material) were prepared the same way by cutting (Secotom-50; Struers, Ballerup, Denmark) the CAD/CAM blocks into standardized

pieces of 1.5 mm thickness under water-cooling. EX specimens required a firing post processing step and were crystallized at 840°C according to the manufacturer's instructions (Programat EP 5000, Ivoclar Vivadent, Schaan, Liechtenstein). All specimens were embedded in acrylic resin (Scandi Quick A and B, ScanDia, Hagen, Germany). Thereafter, all specimens were polished (Tegramin-20; Struers) in 4 steps with a series of silicon carbide papers (SiC) from P500, P1200, P2000 up to P4000 under water-cooling. Specimens were cleaned with distilled water in an ultrasonic bath (Ultrasonic T-14; L&R Manufacturing Co, New Jersey, USA) for 5 min.

2.2 Measurements of Martens hardness

Four specimens of each material were initially measured (n=10 for each material) and then stored in water at 37 °C. After 30, 60, 90, 120 days, the Martens hardness parameters were determined again (n=10 for each material). After 120 days, all specimens were additionally thermo cycled 30,000 times (5/55 °C, 30 s dwell time) and measured again (n=10 for each material).

Martens hardness parameters were determined using testing machine ZHU 0,2 (Zwick Roell, Ulm, Germany). For the test cycle, a Vickers diamond indenter (α=136°) was mounted. The test procedure was force controlled. All specimen surfaces were loaded with 5 N for 10 s. The minimum penetration depth was always > 5 µm. All values presented in this paper are calculated as mean of 10 indentations. For that, 10 measurements were conducted for each group resulting in overall 600 Martens hardness measurements. Martens hardness indentations were set on different pre-defined lines marked on specimen's surfaces to avoid repeated and invalid measurements in same surface area. The load-displacement curves were monitored.

Based on that, the Martens hardness (HM) and the indentation modulus (E_{IT}) were calculated (testX-pert V12.3 Master, Zwick, Ulm, Germany) using the formulas given in the ISO 14577-1 specification.

The HM is defined as the ratio of maximum load F_{max} and the corresponding contact area A at the time of the maximum load. The following equation was used to compute HM:

$$HM = {}^{F_{max}}/_{A_S(h)}$$

With F_{max} in N, $A_S(h)$ in mm

H_{IT} and E_{IT} are representations of the resistance against plastic deformation. The indentation modulus E_{IT} is comparable with the Young's modulus (ISO, 2002) and was calculated as follows:

$$E_{IT} = (1 - \nu_S^2)\left(\frac{2\sqrt{A_P(h_c)}}{\sqrt{\pi}\,S} - \frac{(1-\nu_i^2)}{E_i}\right)^{-1}$$

With E_i (elastic modulus of indenter) in N/mm², $A_p(h_c)$ (projected contact area under load) in mm², v_s and v_i Poisson`s ratio with v_s = 0.4 (Greaves et al.,2011) and v_i = 0.3, S (contact stiffness evaluated from the force removal curve)

2.3 Microstructure and element analysis

One specimen of each material was prepared for microstructure analysis and a second specimen of each material was prepared for element analysis. EX, EC and VE specimens were etched with hydrofluoric acid (Ultradent Porcelain Etch, 9 % buffered hydrofluoric Acid, Ultradent Products, South Jordan UT, USA) for 20 s (EX) and 60 s (EC and VE). Scanning electron microscopy (SEM) analyses was performed using a Zeiss Supra V50 FESEM (Carl Zeiss, Oberkochen, Germany). For microstructure

analysis, specimens were dried and sputtered with gold (Sputter SCD 030, Balzers Union, Balzers, Liechtenstein) to build a layer of approximately 10 nm. Acceleration voltage of 10 kV was used. For elemental analysis, specimens were sputtered with a carbon layer of 12 nm (Baltec Med 020, Balzers Union, Liechtenstein). The analysis was performed using energy-dispersive X-ray-detector of the Supra V50 SEM (Carl Zeiss, Oberkochen, Germany). Acceleration voltage of 12 kV was used.

2.4 Statistical analysis

The measured data were analyzed using descriptive statistics such as mean and standard deviation. Normality of data distribution was tested using the Kolmogorov-Smirnov test. Multifactorial ANOVA followed by the Tukey-HSD post-hoc test was computed to determine the significant differences and impact of parameters on the Martens hardness parameter results. Statistical differences between the tested materials were assessed using the Kruskal-Wallis-H. For pairwise comparison of groups, the Mann-Whitney-U-Test was performed. Results of statistical analyses with p-values smaller than 0.05 were considered as statistically significant (IBM SPSS Statistics v24.0, IBM, Armonk, North Castle, NY, USA).

3 Results

The highest influence on the Martens hardness parameters was exerted by the material (partial eta squared HM: $\eta_P^2 = 0.938$, $p<0.001$; H_{IT}: $\eta_P^2 = 0.967$, $p<0.001$; E_{IT}: $\eta_P^2 = 0.881$, $p<0.001$), followed by the aging duration (HM: $\eta_P^2 = 0.108$, $p<0.001$; E_{IT}: $\eta_P^2 = 0.074$, $p<0.001$). The effect of the binary combinations of the two parameters was also significant (HM: $\eta_P^2 = 0.0064$, $p=0.005$). Except, no statistical differences were observed for the interaction of both parameters for E_{IT} ($\eta_P^2 = 0.030$, $p=0.121$).

Figures 1 and 2 show the progression of the Martens hardness HM and the Indentation Modulus E_{IT} as a function of storage time for all materials tested. Figures 3 and 4 represent HM respectively E_{IT} before and after thermo cycling.

In general, the group of unfilled polymers or ultra-low filled composite (CT, TC, BC) followed by low and compact filled resin composites (AH, EM, KA, LU) showed the lowest HM and E_{IT} values ($p<0.001$). The highest values presented ceramics (EX, EC) followed by hybrid material VE ($p<0.001$).

Within the ceramics, EX showed significantly higher Martens hardness parameters than EC. EX specimens without artificial aging presented the overall highest HM and E_{IT} values ($p<0.001$). For EC, thermo cycled specimens showed significantly lower HM and E_{IT} than specimens after water storage ($p<0.001$).

For VE, thermo cycled specimens showed significantly lower HM and E_{IT} than specimens after water storage ($p<0.001$).

Compact filled resin composites LU and EM showed significantly higher HM than KA and AH ($p<0.001$). For E_{IT}, the lowest values were observed for KA, followed AH ($p<0.001$). The highest E_{IT} values were measured for EM followed by LU ($p<0.001$).

Thermo cycled LU showed significantly lower HM and E_{IT} than after water storage or without artificial aging ($p<0.001$).

Among the unfilled polymers or ultra-low filled composite, BC followed by TC showed significantly lower HM than CT ($p<0.001$). CT presented higher E_{IT} compared to BC and TC ($p<0.001$).

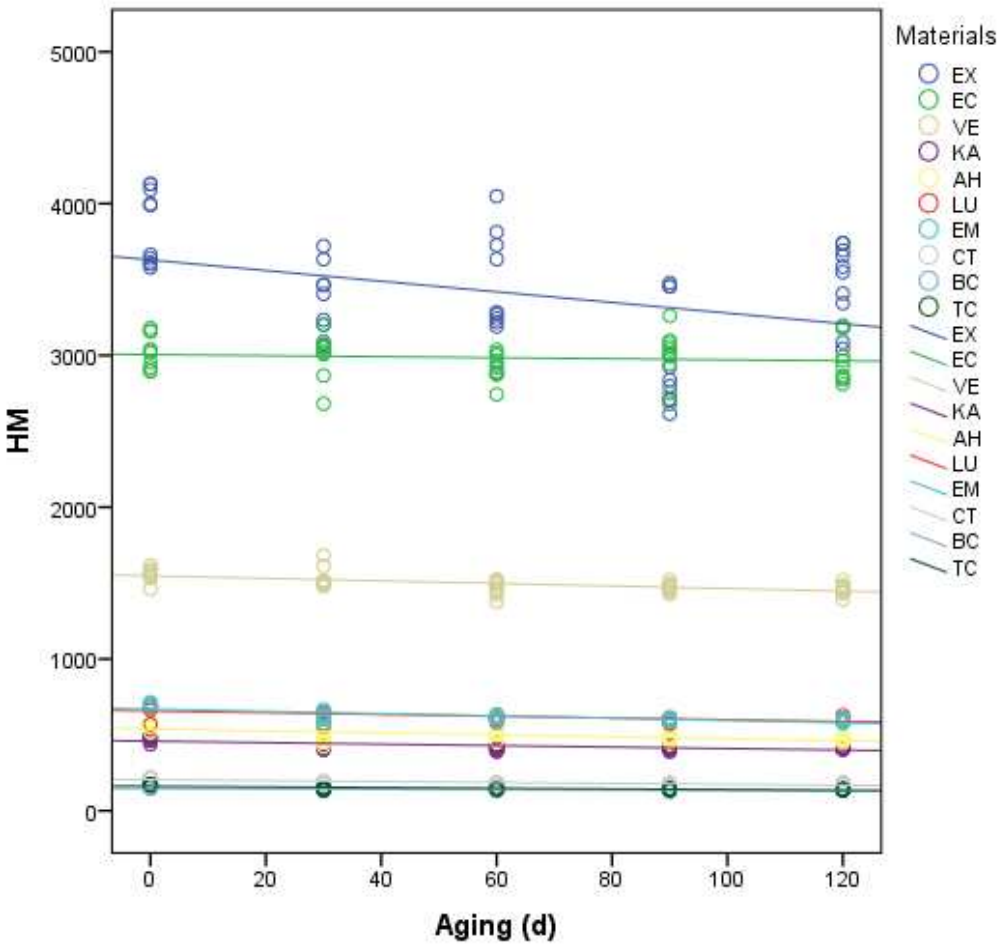


Figure 1: Scatterplot for Martens hardness values (N/mm²)

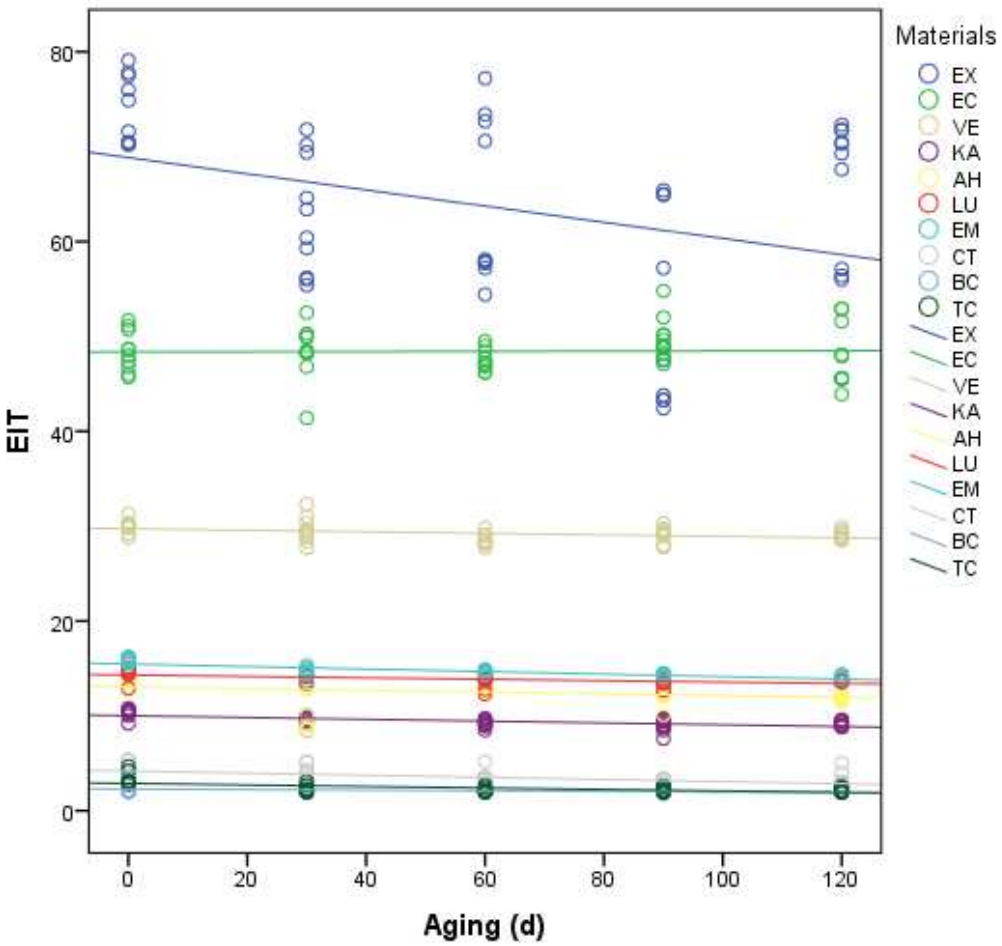


Figure 2: Scatterplot for indentation modulus values (N/mm²)

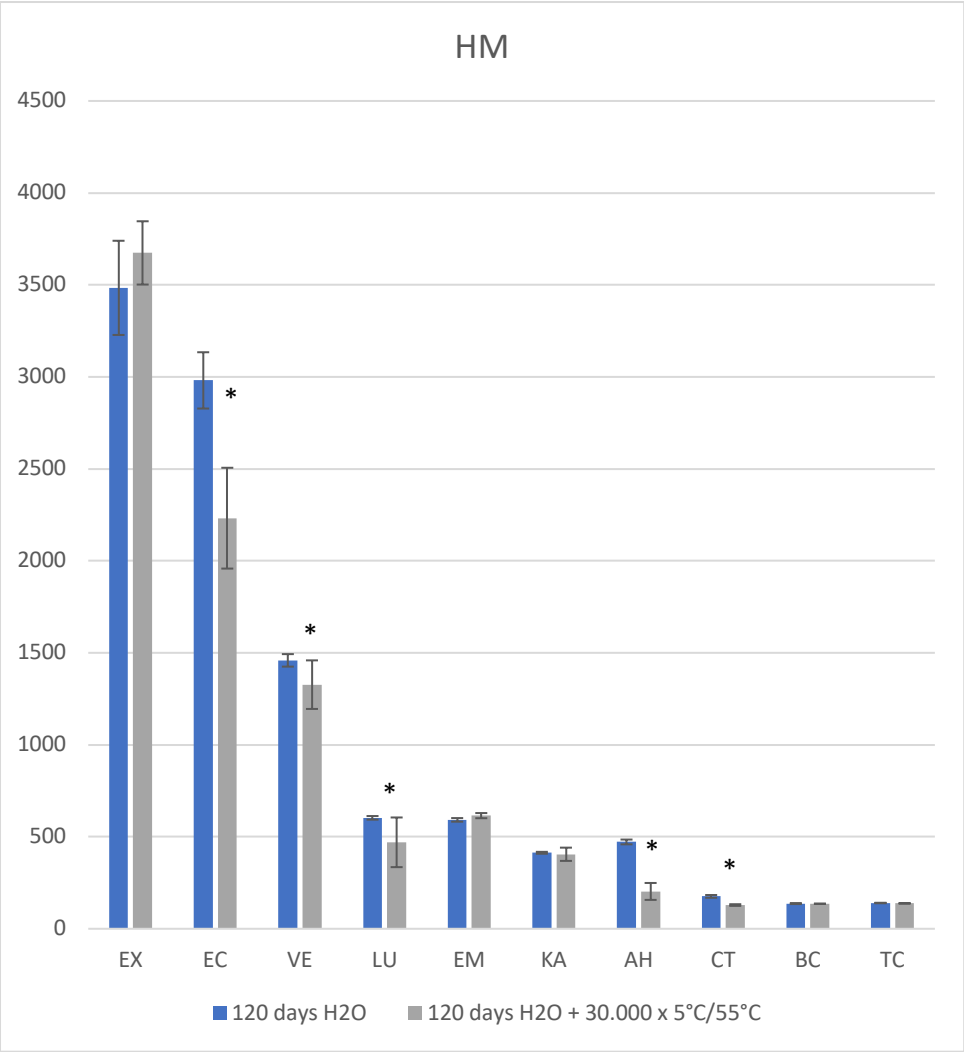


Figure 3: Martens hardness HM in N/mm² after 120 days water storage at 37 °C and Martens hardness after additional thermo cycling, asterisk (*) indicates statistically significant differences between groups before and after thermos cycling

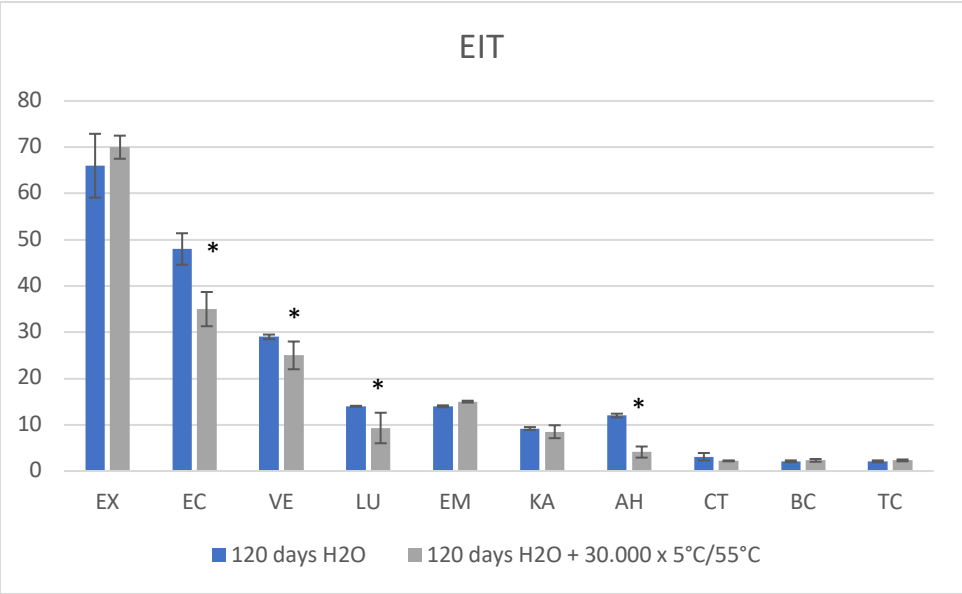


Figure 4: Indentation modulus E_{IT} in N/mm² after 120 days water storage at 37 °C and Indentation modulus after additional thermo cycling; asterisk (*) indicates statistically significant differences between groups before and after thermos cycling

3.4 SEM structure and element analysis

Among ceramics, EX showed high density of distribution of crystallites, in contrast EC showed smaller crystallite structures and a higher content of an amorphous glass phase. EC had more voids in the structure than EX. The hybrid material VE showed a relatively smooth surface with massive flaws and volume defects, Filler particles were not apparent. Comparing the SEM images of low and compact filled resin composites revealed big differences in shape, size and distribution of filler particles (Fig. 5). LU and EM showed insular areas with high filler density, i.e. no compact fillers of that size but filler agglomerates, surrounded by areas with lower filler density. EM showed voids in surrounding areas whereas LU did not. Small fillers of KA were not visible at the selected magnification for structure analysis but element distribution in the EDX

analysis provides evidence of the fillers and their homogeneous distribution within the material. Moreover, KA showed large areas (pre-polymers) of same appearance. For AH, large irregular shaped compact fillers with size of up to approximately 10 µm were detected.

Within the unfilled polymers and ultra-low filled composite, BC and TC showed homogeneous topography without voids or morphological defects while CT showed spherical areas of widely varying extension that were obviously well embedded in matrix material.

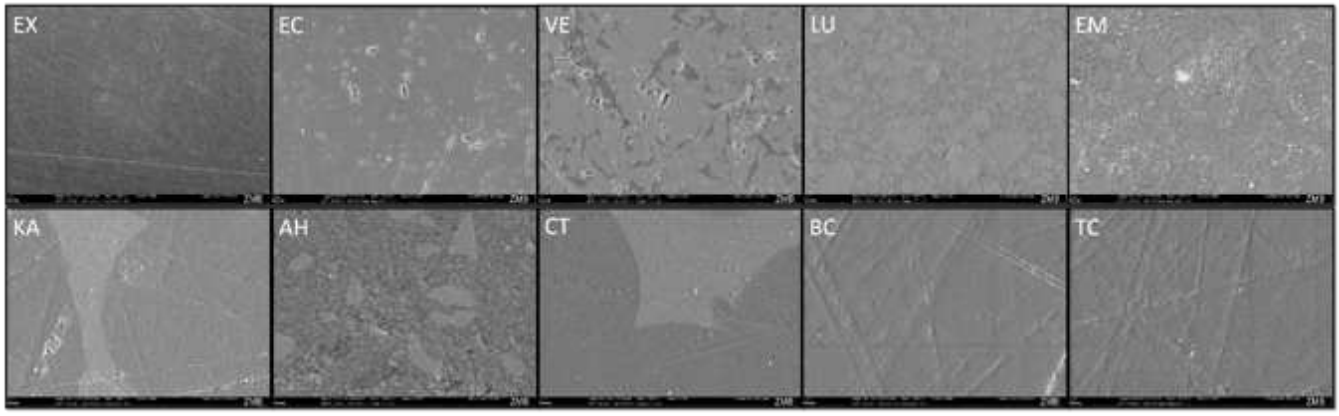


Figure 5: SEM images of material surfaces

EDX Analysis

Element quantification is shown for each material in Table 2. Based on the numbers, it can be stated that AH has aluminosilicate glass fillers, KA only aluminum oxide fillers, LU contains no aluminum oxide particles. Element distribution images revealed mostly a uniform distribution of fillers with two exceptions. CT had fine dispersed fillers in surrounding material but not in pre-polymers (Fig. 6). EM consisted of different types of filler particles – fine dispersed silica, silica clusters (agglomerates) and probably barium-aluminum-fluorosilicate.

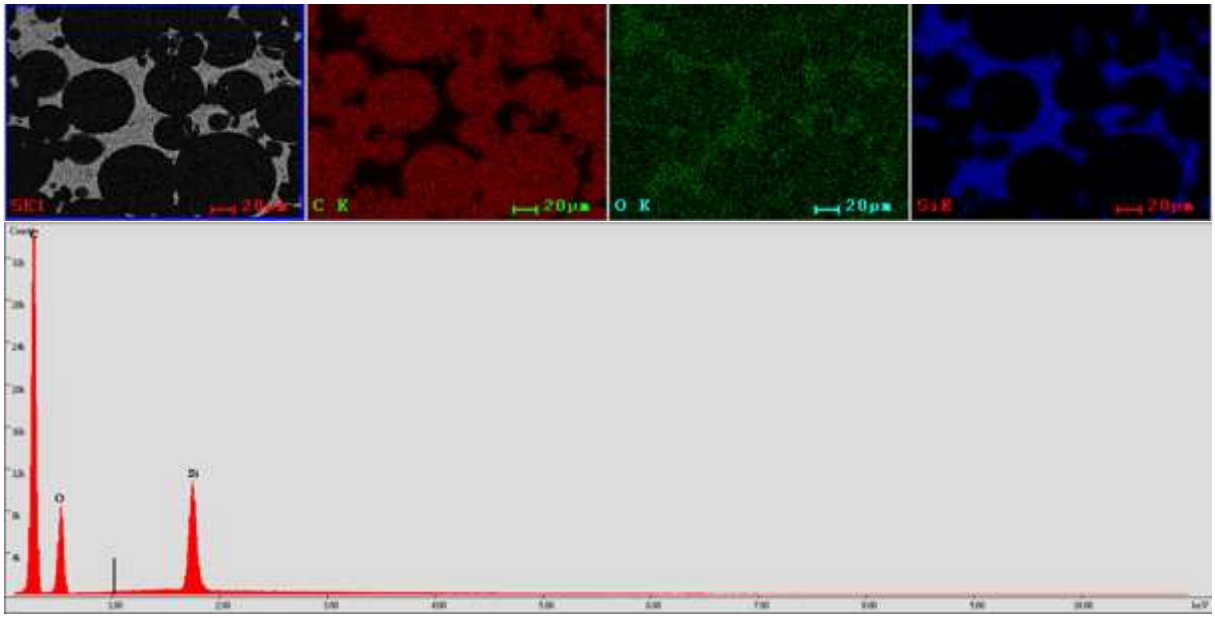


Figure 6: EDX spectrum and element mapping of CT

Table 2: Results of element analysis by EDX, element quantification is shown for each material

Material Group	Material	Element in Weight %							
		C	O	Al	Si	P	Ba	Na	K
Ceramics	EX	21	36	2	36	1			3
	EC	10	37	10	31			3	9
Hybrid	VE	29	35	8	20			5	3
Compact filled composites	LU	33	34		23	6			
	EM	34	31	3	24	3	5		
Low filled composites	KA	42	27	31					
	AH	42	29	5	23				
Unfilled polymers/ult	CT	72	22		6				

ra-low filled composite	BC	76	24						
	TC	76	24						

4 Discussion

4.1 Behavior of CAD/CAM restorative materials

The results of this study revealed that all CAD/CAM restorative materials behave elastic-plastic to a certain extent but show differences in mechanical properties. The basic output of the instrumented indentation testing - the load-displacement curves - discloses typical differences characteristic for the different material classes regarding maximum indentation depth h_{max}, creep C_{IT} (indentation depth changes at dwell with constant maximum load), elastic reverse deformation work W_e (integrated area below unloading curve), and permanent irreversible deformation work W_{total} (integrated area below loading curve) (Fig. 7). For polymers and polymeric composites with dispersed fillers, it can be concluded that with increased filler content, the creep decreases while the mechanical work of indentation decreases with an increasing ratio of $\eta_{IT}=f(W_e/W_{total})$. The area between the loading and unloading curve ($W_p=1-\eta_{IT}$) quantifies the permanent damages. In Figure 7 it can also be seen that permanent damages decrease within and over the material classes with the increase of inorganic fraction of the materials. The root cause for this damage is most probably different for the material classes. For unfilled polymers, the dominant mechanism is presumably plastic yielding. As microscopic images of the indentation areas suggest, the dominant mechanism for ceramics and the hybrid material is microfracturing. The hybrid material (VE) shows higher and the ceramic materials (EX, EC) show highest mechanical properties represented in Figure 7 by steeper gradients of loading and unloading curves resulting in less indentation work. Ceramics show low amount of plastic

deformation (low η_{IT}). The curve peaks without a plateau indicate virtually no creep under indention load.

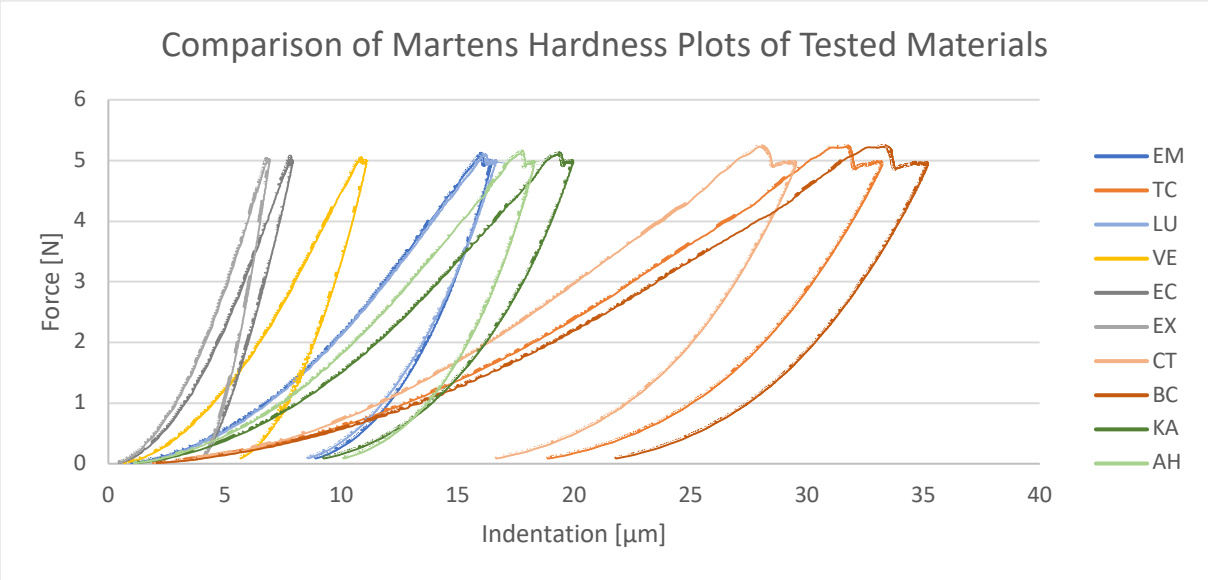


Fig. 7: Typical load-displacement curves of instrumented indentation to assess HM and E_{IT} for materials tested. Materials belonging to one material class are presented in shades of same color.

Aging due to long-term storage in water at body temperature and thermo cycling affect the materials differently. Even within one material group, the materials do not behave the same. It cannot be concluded from the material group whether the material is prone to alter the mechanical properties during aging or not. The null hypotheses that the tested material groups show similar mechanical properties and that aging does not influence the mechanical properties of CAD/CAM materials needs to be rejected. In accordance to Ruse & Sadoun (2014) and based on the findings of this study, it can be reemphasized that the advantages and the disadvantages of the different available CAD/CAM materials should be considered before deciding a patient treatment. The current CAD/CAM resin composites have advantageous regarding machinability, intra-oral repair ability and show a sufficient mechanical behavior and esthetics for most

indications but they do not reach the flexural strength of ceramics. On the other hand, ceramics are brittle materials and one major reason for clinical failures is the fracture of restorations (Donovan 2008).

The structural analysis confirmed that all resin composites are composed of dispersed fillers in a resin matrix. The differences lay in the size, shape, and kind of fillers. In contrast, VE showed another microstructure. According to the manufacturer, it is composed as a polymer infiltrated ceramic network. The hybrid VE differed significantly from the behavior of ceramics and did not show the level of ceramic for tested parameters. VE showed good stability in isotherm water storage but the mechanical properties were negatively affected by thermo cycling. It can be speculated that the thermo cycling induced stress at the network interfaces due to differences in the thermal expansion coefficient. The findings are in accordance to Sen et al. (2015) who also found a decrease of mechanical properties for VE. The mechanical properties of EC, LU, AH, and CT were also negatively affected by thermo cycling. The two materials within the group of compact filled composites showed very similar initial mechanical behavior and both behaved similar when stored in water but responded differently to thermo cycling. EM showed stable behavior whereas the mechanical properties of LU dropped drastically. In case of LU, one explanation might be the hydrolysis of silane coupling agents due the water. It may also be concluded that the kinetic in water uptake is similar above all resin composites. After a first slight drop of mechanical properties which can be associated with water uptake, longer storage in water did not deteriorate the mechanical behavior. Equilibrium stage was reached after 30 days. Liebermann et al. (2016) reported comparable results when they tested long term aging in different storage media.

Within the group of unfilled polymers/ultra-low filled composites, the results revealed that CT with an ultra-low filler content of approximately 6 w% to 8 w% showed significantly higher mechanical properties with a reduced creep compared to completely unfilled formulations. Another difference of CT compared to BC and TC is the morphology with embedded prepolymer spheres in the surrounding resin matrix. The inorganic fillers are embedded in the surrounding resin matrix solely.

4.2 Study setup

Restorative materials are exposed in vivo to a wet oral environment. Therefore, it can be stated that water storage is relevant for simulating the wet environment in-vitro. Besides artificial saliva, ethanol is another standard storage medium used in aging studies. Storing resin based composites in ethanol results in a more pronounced decrease of mechanical strength (Schmidt & Ilie, 2011; Randolph et al., 2016). Ethanol is a good dimethacrylate solvent (Miranda, 2011) and can soften the matrix (deMoraes, 2014). Ethanol might be suitable for simulating nutrition effects like certain beverages and dental cosmetic products have (Al Badr & Hassan, 2017) but from author's perspective, the clinical relevance of storing dental restorative material for a longer time of period in ethanol is questionable.

Thermal cycling is widely used to simulate aging of dental restorative materials but there is a lack of standardization in the protocols regarding number of cycles, dwell time and temperature (Morresi et al., 2014). Temperatures of 5 °C-55 °C are considered as the closest to the physiological situation (ISO,1994). The above-mentioned circumstances were taken into consideration for the design of the present study with 5-55 °C as established in ISO standard and 30,000 cycles which might represent 3 years (Gale, 1999).

The Martens hardness is an established method to characterize mechanical behavior of dental restorative materials. Ilie et al. (2005) especially stated that resin composites are visco-elastic bodies and hence, E_{IT} represents correct values instead of Young`s modulus calculated on basis of stress-deflection diagrams. Since the values of Martens hardness parameters are influenced by set parameters of the test and since these set parameters differ among publications, the results are hardly comparable (Czichos, 2011). In the current study, a setup has been found to be universally suitable for all restorative materials tested which covered the entire spectrum of material classes used for chairside CAD/CAM restorations. The indentation depth was at least 5 µm as demanded in the ISO standard. At the same time cracks along the diagonals of the indentation could also not be observed. All groups showed low variances mostly in the range of 3 to 15 % within one measurement series indicating the suitability of the Martens hardness measurement setup for all materials including resin composites with dispersed fillers.

Considering all these facts, the method with the parameters used can be assessed as valid to characterize the aging behavior of CAD/CAM restorative materials. The analysis of the microstructure via SEM and EDX helps to understand the results of Martens hardness measurements and the characteristic mechanical behavior of different CAD/CAM materials.

5 Conclusions

Within the limitations of this in vitro study, it can be concluded that:

- The mechanical properties of CAD/CAM restorative materials vary widely depending on the material class. Neither the hybrid material nor resin composites reach that level of ceramics, neither initially nor after different aging.

- Water storage at elevated temperature of 37 °C and thermo cycling between 5-55 °C reveal different effects on materials. For some materials, the mechanical properties drop down after thermo cycling. For a good estimation of the long-term stability of dental restorative materials in the clinical situation, artificial aging tests should include thermo cycling. Thermo cycling reflects the clinical situation better than isothermal storage.

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